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Mononuclear bromide complexes of Sb(V): crystal structures and thermal behaviour

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ABSTRACT

Reactions of Sb_2O_3 dissolved in HBr/Br_2 and bromides of pyridinium-derived cations result in mononuclear complexes of Sb(V) – (cation)[$SbBr_6$] (cation = 2-chloropyridinium (**1**), 2-bromopyridinium (**2**)). Thermal behaviour of **1** and **2**, as well as similar previously reported complexes Et_4N [$SbBr_6$] (**3**) and (N-EtPy)[$SbBr_6$] (**4**), was studied and discussed.

1. Introduction

Halometalates of late transition (Cu, Ag) and post-transition metals (in particular, Pb, Sb and Bi) attract much attention due to a number of promising features [1,2]. Among those, there are photochromism occurring in viologen salts [3–5], thermochromism [6,7], ferroelectricity and ferroelasticity [8–12], unusual color changes induced by surface interaction with solvent [13], photocatalytic activity [14–18] etc. Besides, halometalates demonstrate extraordinary structural diversity: they can reach nuclearity of up to 8 Bi (in discrete anions) [19–28], as well as form various polymers [29–34], making them interesting objects in terms of structural chemistry. Within the last years, the special interest has been focused on the studies related to their use in photovoltaic (so-called "perovskite-type") devices. Although most efforts were concentrated on Pb(II) iodides, more recent articles display a clear trend in expansion on other halometalates (in particular, Bi(III), Sn(II)), targeting more stable light absorbers [35].

Very recently it was shown [36] that bromoantimonates (V) can be successfully applied in design of solar cells. Therefore, considering the great importance of this field, aggregation of novel chemical data on these systems is needed. Analyzing the earlier articles, we found that the only systematic studies of such complexes were undertaken over 40 years ago by Jacobson et al. [37–40] Their reports were mostly concentrated on structural analysis. The most interesting finding was that the reactions of the "Sb_2O_3 + HBr + Br_2 + $CationBr_x$" type can lead to the products of several different types. Commonly, a partial or complete oxidation of Sb(III) to Sb(V) occurs during the reaction, yielding either mixed-valent Sb(III)/Sb(V) or pure Sb(V) complexes, in some cases accompanied by incorporation of {Br_3} units into the structure. The initial stoichiometry affects the yield, but not the stoichiometry of the resulting products, and the formation of certain structural type seems to be purely cation-dependent.

Aiming at resumption and expansion of these studies, we have decided to expand the range of cations used in these reactions, and to investigate relevant physical properties, both of new compounds and some of those already reported by Jacobson et al. In this work we present two novel complexes with [$SbBr_6$]$^-$ anion: (2-XPyH$^+$)[$SbBr_6$] (X = Cl (**1**), Br (**2**)), which were characterized by X-ray diffractometry. Additionally, we report and compare thermal behaviour of **1**–**2** and two known hexabromoantomonates: Et_4N [$SbBr_6$] (**3**) [40] and (N-EtPy)[$SbBr_6$] (**4**) [36].

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